Project Report: Electrochemical isotope effects with applications to stable isotope fractionation in transition metals

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Project Progress

Our project to identify the underlying mechanisms of stable isotope fractionation in biological systems is moving forward. We have recently collected evidence that there is a charge−transfer contribution to kinetic stable isotope fractionation that should have significance for the biological fractionation of ^{56}Fe, ^{57} Fe, and ^{54} Fe and other transition metal isotopes. We performed a series of electroplating experiments that demonstrated a voltage−dependent isotope fractionation during reduction of Fe^{+2} to Fe metal, with magnitudes covering the range observed in natural biotic and abiotic systems. We have developed a theory, based on the fundamental theory for electron transfer developed previously by Marcus, that accounts for the observed voltage dependent fractionation. The theory is general and makes a broad−based series of predictions concerning stable isotope fractionation in a wide variety of charge−transfer reactions. Our results demonstrate a specific mechanistic origin of stable isotope fractionations in Fe during redox phenomena.

Armed with this new tool, we are now in position to use observed stable isotope fractionations as markers for the specific driving forces in charge−transfer reactions, including biologically mediated electron exchange reactions. In particular, the theory makes testable predictions about the isotope fractionation to be observed based on the ligands that surround a given transition metal during the electron−transfer processes. We are presently expanding our experiments to test these predictions.

Highlights

- We have established the first combined electrochemical/geochemical techniques to examine stable isotope fractionations due to charge−transfer processes, and have used this technique to establish voltage−dependent fractionation for Fe (manuscript in preparation).
- We have developed a theory that predicts stable isotope fractionation as a function of electron−transfer driving force. This theory is an extension of the Marcus theory to isotope specific reaction rates

(manuscript in preparation).

Roadmap Objectives

- ***Objective No. 3.1:*** Sources of prebiotic materials and catalysts
- ***Objective No. 4.1:*** Earth's early biosphere
- ***Objective No. 4.2:*** Foundations of complex life
- ***Objective No. 6.1:*** Environmental changes and the cycling of elements by the biota, communities, and ecosystems
- ***Objective No. 7.1:*** Biosignatures to be sought in Solar System materials